This is a Class 1 exam

Lebanon Evangelical School
for Boys and Girls
Loueizeh - Baabda

Stage Exam 01

11NOV2022

Do NOT write in this box. Your MARK will be placed here.

Subject :	A Level : Chemistry 2	
Class :	12A	
Teacher :	Mrs. Saydeh Nasrallah	
Duration :	2 hours	
Your name :		*Time taken to complete exam*
Your Class :		
Exam Room :		
How many sheets, including cover sheet :		

- Do not open this paper until the teacher in charge instructs you to do so.
- The most important thing to remember in taking an exam is NEVER PANIC.
- If you are caught cheating in this exam, you will be awarded zero for ALL exams that are taken on this day.

SECTION A

Answer ALL the questions in this section.
You should aim to spend no more than 20 minutes on this section.
For each question, select one answer from A to D and put a cross in the box.
If you change your mind, put a line through ☒ the box and then mark your new answer with a cross. ☒

1. Ammonium nitrate is very soluble in water.

$$NH_4NO_3(s) + aq \rightarrow NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H = +25.8\,kJ\,mol^{-1}$$

What is the best explanation for this?

☐ **A** all ammonium salts are soluble in water
☐ **B** the activation energy of the reaction is very low
☐ **C** the enthalpies of hydration of the ions are very exothermic
☐ **D** the entropy change of the system, ΔS_{system} , is positive

(Total for Question 1 = 1 mark)

2. The standard molar entropy, S, of a substance

☐ **A** is not affected by changes of state or changes in temperature
☐ **B** only changes when the temperature changes
☐ **C** only changes when the substance changes state
☐ **D** changes when the temperature changes and when the substance changes state

(Total for Question 2 = 1 mark)

3. At 25 °C, the pH of pure water is 7.00 and at 100 °C, the pH of pure water is 6.14.
What can be deduced from this information?

		Enthalpy change of dissociation of water	Concentration of hydrogen ions
☐	**A**	endothermic	higher at 100 °C than at 25 °C
☐	**B**	endothermic	lower at 100 °C than at 25 °C
☐	**C**	exothermic	higher at 100 °C than at 25 °C
☐	**D**	exothermic	lower at 100 °C than at 25 °C

(Total for Question 3 = 1 mark)

4. The equation for the precipitation of lead(II) chloride is shown.

$$Pb^{2+}(aq) + 2Cl^{-}(aq) \rightleftharpoons PbCl_2(s)$$

What are the units of the equilibrium constant, Kc?

☐ **A** $dm^9.mol^{-3}$
☐ **B** $dm^6.mol^{-2}$
☐ **C** $mol^2.dm^{-6}$
☐ **D** $mol^3.dm^{-9}$

(Total for Question 4 = 1 mark)

5. The reaction shown is at equilibrium. The forward reaction is endothermic.

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

(a) Which will **increase** when the temperature is lowered?

(1)

☐ **A** the mole fraction of carbon dioxide
☐ **B** the partial pressure of carbon monoxide
☐ **C** the rate of the backward reaction
☐ **D** the value of Kp for the forward reaction

(b) At 680 °C and 1 atm, 52.6 % of the molecules in the gas mixture are carbon monoxide. What is the partial pressure of carbon dioxide, in atmospheres?

(1)

☐ **A** 0.237
☐ **B** 0.263
☐ **C** 0.474
☐ **D** 0.526

(Total for Question 5 = 2 marks)

6. Experimental lattice energy values determined using the Born-Haber cycle often differ from calculated theoretical values. The ionic radii and charges of some ions are shown.
P, Q, R and S are **not** the chemical symbols of the elements.

Ion	Ionic radius / nm
P^+	0.076
Q^+	0.167
R^-	0.133
S^-	0.220

Which of these compounds would be expected to show the largest percentage difference between the experimental and theoretical lattice energies?

☐ **A** **PR**
☐ **B** **PS**
☐ **C** **QR**
☐ **D** **QS**

(Total for Question 6 = 1 mark)

7. A series of experiments was carried out to determine the rate constant, k, of the reaction between bromate(V) ions and bromide ions at different temperatures, T.
A graph of $\ln k$ was plotted against $1/T$. The gradient of the line was −4670 K.
The Arrhenius equation may be written as

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + constant \qquad R = 8.31\, J\, mol^{-1} K^{-1}$$

What is the activation energy of this reaction?

☐ **A** $+38.8\, kJmol^{-1}$
☐ **B** $+38.8\, J\, mol^{-1} K^{-1}$
☐ **C** $+562\, Jmol^{-1}$
☐ D $+562\, Jmol^{-1} K^{-1}$

(Total for Question 7 = 1 mark)

8. Solid vanadium(V) oxide catalyses the equilibrium shown.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196\,kJ\,mol^{-1}$$

Which statement is correct?

- ☐ **A** vanadium(V) oxide is a homogeneous catalyst
- ☐ **B** decreasing the pressure would increase the equilibrium yield of sulfur trioxide
- ☐ **C** increasing the surface area of the catalyst would increase the equilibrium yield of sulfur trioxide
- ☐ **D** decreasing the temperature would increase the equilibrium yield of sulfur trioxide

(Total for Question 8 = 1 mark)

9. What is the pH of a $0.27\,mol\,dm^{-3}$ aqueous solution of sodium hydroxide?
[$K_w = 1.0 \times 10^{-14}\,mol^2\,dm^{-6}$ at 298 K]

- ☐ **A** 0.57
- ☐ **B** 13.43
- ☐ **C** 13.73
- ☐ **D** 14.57

(Total for Question 9 = 1 mark)

10. Propanone reacts with iodine in the presence of a sulfuric acid catalyst.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

The rate equation for this reaction is:

$$\text{rate} = k[H^+][CH_3COCH_3]$$

Two experiments were carried out. In both experiments the concentration of propanone and iodine remained the same but the concentration of the sulfuric acid was changed.
The initial rate in the first experiment was three times faster than the initial rate in the second experiment.
In the first experiment the initial pH was 1.50
What is the initial pH in the second experiment?

- ☐ **A** 1.02
- ☐ **B** 1.98
- ☐ **C** 2.28
- ☐ **D** 4.50

(Total for Question 10 = 1 mark)

11. The water gas reaction is used in the manufacture of hydrogen.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad \Delta H = +131.2\,kJ\,mol^{-1}$$

(a) What is the equilibrium constant, K_c, for this reaction?

(1)

☐ A $K_c = [CO][H_2]$

☐ B $K_c = \dfrac{[CO][H_2]}{[C]}$

☐ C $K_c = \dfrac{[CO][H_2]}{[H_2O]}$

☐ D $K_c = \dfrac{[CO][H_2]}{[H_2O][C]}$

(b) What happens to the equilibrium constants of the forward and reverse reactions when the temperature is **increased**?

(1)

	K_c of forward reaction	K_c of reverse reaction
☐ A	increases	increases
☐ B	increases	decreases
☐ C	decreases	increases
☐ D	decreases	decreases

(Total for Question 11 = 2 marks)

12. The total entropy change, ΔS_{total}, of a reaction at 298 K is $-85.0\,J\,K^{-1}\,mol^{-1}$.

What is the value of the equilibrium constant for this reaction at 298 K?

[$R = 8.31\,J\,mol^{-1}\,K^{-1}$]

☐ A 3.61×10^{-5}

☐ B 9.07×10^{-1}

☐ C 9.66×10^{-1}

☐ D 2.77×10^{4}

(Total for Question 12 = 1 mark)

13. When ethanoic acid and chloroethanoic acid are mixed, an equilibrium is set up.

$$CH_3COOH + CH_2ClCOOH \rightleftharpoons CH_3COOH_2^+ + CH_2ClCOO^-$$

The Brønsted-Lowry acids in this equilibrium are

☐ **A** CH_3COOH and $CH_2ClCOOH$
☐ **B** CH_3COOH and $CH_3COOH_2^+$
☐ **C** $CH_2ClCOOH$ and $CH_3COOH_2^+$
☐ **D** $CH_3COOH_2^+$ and CH_2ClCOO^-

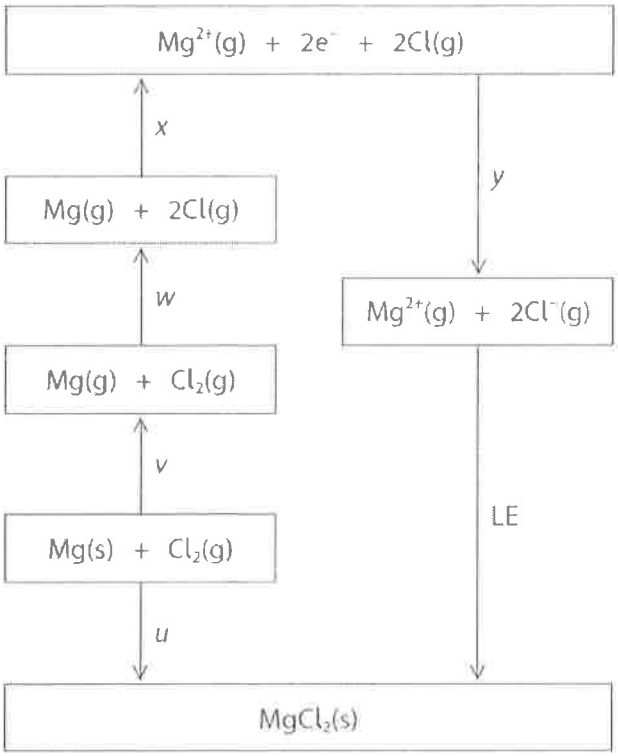
(Total for Question 13 = 1 mark)

14. An ionic solid dissolves in water.
Which of the following statements about the signs of these standard enthalpy changes is possible?

	$\Delta H^{\ominus}_{solution}$	$\Delta H^{\ominus}_{hydration}$	Lattice energy
☐ **A**	negative	negative	positive
☐ **B**	positive	negative	negative
☐ **C**	negative	positive	negative
☐ **D**	positive	positive	positive

(Total for Question 14 = 1 mark)

15. The diagram shows the Born-Haber cycle for magnesium chloride.



(a) Which of these is the electron affinity of chlorine?

(1)

☐ **A** y
☐ **B** y/2
☐ **C** (w + y)
☐ **D** (w + y)/2

(b) Which expression gives the lattice energy (LE) for magnesium chloride?

(1)

☐ **A** LE = $u - (v + w + x + y)$
☐ **B** LE = $v + w + x + y - u$
☐ **C** LE = $y - u - (v + w + x)$
☐ **D** LE = $v + w + x - y + u$

(c) Which energy change in the cycle does *x* represent?

(1)

☐ **A** the first ionisation energy of magnesium
☐ **B** the second ionisation energy of magnesium
☐ **C** the sum of the first and second ionisation energies of magnesium
☐ **D** the sum of the enthalpy change of atomisation and the first and second ionisation energies of magnesium

(Total for Question 15 = 3 marks)

16. The decomposition of hydrogen iodide at 500 K is an equilibrium reaction.
The equilibrium can be written as two different equations.

Equation 1 $HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$ $\Delta H_1 = +5\,kJ\,mol^{-1}$ $K_{c_1} = 6 \times 10^{-3}$

Equation 2 $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ ΔH_2 $Equilibrium\,constant = K_{c_2}$

Which combination of expressions is correct?

☐ **A** $\Delta H_1 = \Delta H_2$ and $K_{c_1} = K_{c_2}$
☐ **B** $\Delta H_1 = \frac{1}{2}\Delta H_2$ and $K_{c_1} = \frac{1}{2} K_{c_2}$
☐ **C** $\Delta H_1 = \sqrt{\Delta H_2}$ and $K_{c_1} = \sqrt{K_{c_2}}$
☐ **D** $\Delta H_1 = \frac{1}{2}\Delta H_2$ and $K_{c_1} = \sqrt{K_{c_2}}$

(Total for Question 16 = 1 mark)

17. Which reaction has an enthalpy change equal to the enthalpy change of solution of potassium chloride?

☐ **A** 1 mol KCl(s) + 2 mol of $H_2O(l)$ → $K^+(aq)$ + $Cl^-(aq)$
☐ **B** 1 mol KCl(s) + excess $H_2O(l)$ → $K^+(aq)$ + $Cl^-(aq)$
☐ **C** 1 mol KCl(g) + 2 mol of $H_2O(l)$ → $K^+(aq)$ + $Cl^-(aq)$
☐ **D** 1 mol KCl(g) + excess $H_2O(l)$ → $K^+(aq)$ + $Cl^-(aq)$

(Total for Question 17 = 1 mark)

TOTAL FOR SECTION A = 21 MARKS

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

18. The kinetics of the reaction between hydrogen peroxide and iodide ions in the presence of sulfuric acid is investigated.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

(a) First, the concentration of hydrogen peroxide is measured at different times, while keeping the concentrations of iodide and hydrogen ions constant. The following results are obtained.

$t / 10^3 s$	$[H_2O_2]$ / mol dm^{-3}
0	0.20
2	0.14
4	0.09
6	0.06
8	0.04
10	0.03

(i) Plot a graph of $[H_2O_2]$ / mol dm^{-3} against $t / 10^3 s$.

(2)

(ii) Find **two** successive half-lives from your graph.
Show your working on your graph, together with their values.

(2)

(iii) Deduce the order of the reaction with respect to hydrogen peroxide. Justify your answer.

(2)

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(b) The experiment is repeated using an initial rate method.
Mixtures are prepared using $0.10 mol\ dm^{-3}$ solutions of each reactant, $2 cm^3$ of sodium thiosulfate solution mixed with starch and varying amounts of water so that the total volume is always $12 cm^3$.
The time for the mixtures to change colour is recorded and the initial rate calculated.

Run	Volume KI /cm³	Volume H_2O_2 /cm³	Volume H_2SO_4 /cm³	Volume of water /cm³	Initial rate /mol dm^{-3} s^{-1}
1	3.0	3.0	3.0	1.0	1.06×10^{-4}
2	2.0	3.0	3.0	2.0	7.00×10^{-5}
3	1.0	3.0	3.0	3.0	3.50×10^{-5}
4	3.0	3.0	2.0	2.0	1.08×10^{-4}
5	3.0	3.0	1.0	3.0	1.05×10^{-4}

(i) The reciprocal of time can be used as an approximate measure of rate.
What assumption does this approximation depend on?

(1)

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(ii) Use the results in the table to deduce the order of reaction with respect to iodide ions and hydrogen ions.
Justify each answer by referring to relevant data from the table.

(3)

Iodide ions .....

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Hydrogen ions .....

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(iii) Write the overall rate equation for this reaction using your answers to (a)(iii) and (b)(ii).

(1)

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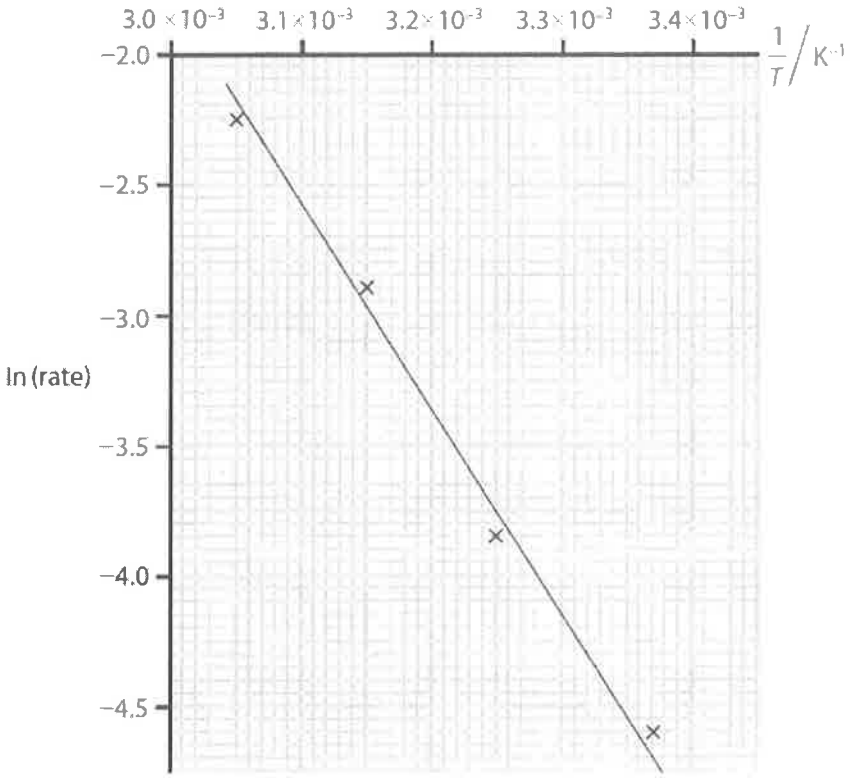
(iv) Calculate the actual concentrations of hydrogen peroxide and iodide ions in the **mixture** used in Run 1 from the table in (b).

(1)

(v) Calculate a value for the rate constant using Run 1 from the table in (b) and your answers to parts (b)(iii) and (b)(iv). Include units for the rate constant.

(2)

(c) (i) The activation energy for this reaction is found by keeping the concentrations of reactants constant and repeating the reaction at different temperatures.
A graph of $\ln(rate)$ of the reaction against reciprocal of temperature is given below.



Calculate the gradient of the graph.
Use your value of the gradient and the equation below to calculate the activation energy of the reaction.

$$\ln(rate) = -\frac{E_a}{R} \times \frac{1}{T} + constant \qquad [\ R = 8.31\ J\ K^{-1}\ mol^{-1}\ ]$$

Include a sign and units with your answer.

(3)

*(ii) If the same reaction is carried out in the presence of a catalyst of ammonium molybdate, the activation energy is found to be much lower.
Sketch a Maxwell-Boltzmann distribution of molecular energies.
Use your sketch to explain why this reduction in activation energy increases the rate of the reaction.

(3)

Explanation

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(Total for Question 18 = 20 marks)

19. This question is about ammonia and ammonium chloride.

(a) Ammonia is produced by reacting nitrogen and hydrogen as shown.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) Write the expression for the equilibrium constant, K_p.

(1)

(ii) An equilibrium was established by mixing nitrogen and hydrogen in a 1:3 ratio by volume, at a temperature of $450\,°C$ and pressure of $200\,atm$.
The equilibrium mixture contained 28% of ammonia and 18% nitrogen by volume.
Complete the table.

(2)

Substance	Mole fraction	Partial pressure / atm
N_2	0.18	
H_2		
NH_3	0.28	56

(iii) Calculate the equilibrium constant.
Give your answer to an appropriate number of significant figures and include units, if required.

(2)

(iv) When the temperature was reduced to 400°C at the same pressure, the equilibrium mixture contained 36% of ammonia.
Explain what can be deduced about this reaction from this information.

(2)

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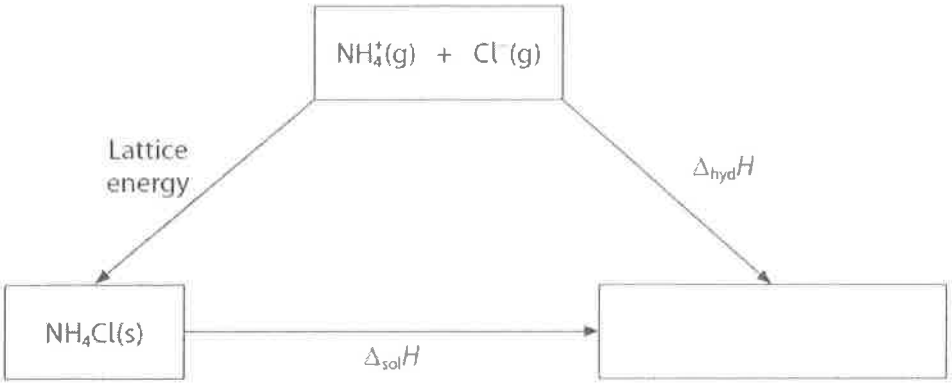
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(b) Ammonium chloride can be produced by reacting ammonia with hydrogen chloride.
Ammonium chloride is a white solid that is very soluble in water.
Hess's Law can be used to calculate the enthalpy of solution of ammonium chloride, using hydration enthalpies and lattice energy.

(i) Complete the Hess cycle by filling in the empty box.

(1)



(ii) Complete the expression for the enthalpy change of solution using the hydration enthalpies and lattice energy.

(1)

$\Delta_{sol}H =$

(iii) Calculate the enthalpy change of solution, using your expression in (b)(ii) and these data.
Enthalpy change of hydration of $NH_4^+ = \quad -307\,kJ\,mol^{-1}$
Enthalpy change of hydration of $Cl^- = \quad -378\,kJ\,mol^{-1}$
Lattice energy of $NH_4Cl = \quad -705\,kJ\,mol^{-1}$

(2)

(iv) A student suggested that the enthalpy change of solution of ammonium bromide would be of a similar magnitude to the enthalpy change of solution of ammonium chloride. Comment on this suggestion in terms of the hydration enthalpies and lattice energies of these two compounds.

(3)

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(c) Write an **ionic** equation to show why aqueous solutions of ammonium ions are acidic. State symbols are not required.

(1)

(Total for Question 19 = 15 marks)

20. This question is about acids and bases.

(a) State what is meant by a Brønsted-Lowry base.

(1)

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(b) Calculate the concentration of hydrogen ions, in $mol\,dm^{-3}$, in a solution with a pH of 9.43

(1)

(c) Write the equation for the dissociation of water.

(1)

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(d) Write the expression of K_w.

(1)

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(e) The ionic product of water, K_w, varies with temperature as shown.

Temperature / °C	K_w / mol^2 dm^{-6}
0	0.11×10^{-14}
10	0.29×10^{-14}
20	0.68×10^{-14}
30	1.47×10^{-14}
40	2.92×10^{-14}
50	5.48×10^{-14}

(i) Determine the value of K_w at 45°C by plotting a suitable graph.
You must show your working on the graph.

(4)

K_w at 45°C = ...

(ii) The ionic product of water at 30°C is $1.47 \times 10^{-14} mol^2 dm^{-6}$.
Calculate the pH of water at this temperature.

(3)

(f) Calculate the pH of the solution formed when $51.2\,cm^3$ of $0.927\,mol\,dm^{-3}$ NaOH(aq) is mixed with $40.4\,cm^3$ of $0.370\,mol\,dm^{-3}$ H_2SO_4(aq).
[Ionic product of water $K_w = 1.00 \times 10^{-14}\,mol^2\,dm^{-6}$]

(6)

(Total for Question 20 = 17 marks)
TOTAL FOR SECTION B = 52 MARKS

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

21. The equation for the formation of ammonia in the Haber Process is shown

$$\tfrac{1}{2}N_2(g) + 1\tfrac{1}{2}H_2(g) \rightleftharpoons NH_3(g)$$

(a) At 298K the standard entropy change of the system, $\Delta S^{o}_{system} = -98\,J\,K^{-1}\,mol^{-1}$.

Calculate the standard entropy of one mole of ammonia.
Use the value of ΔS^{o}_{system} and the data in the table.

Substance	Standard molar entropy, S^{o}/ $JK^{-1}mol^{-1}$
N_2	192
H_2	131

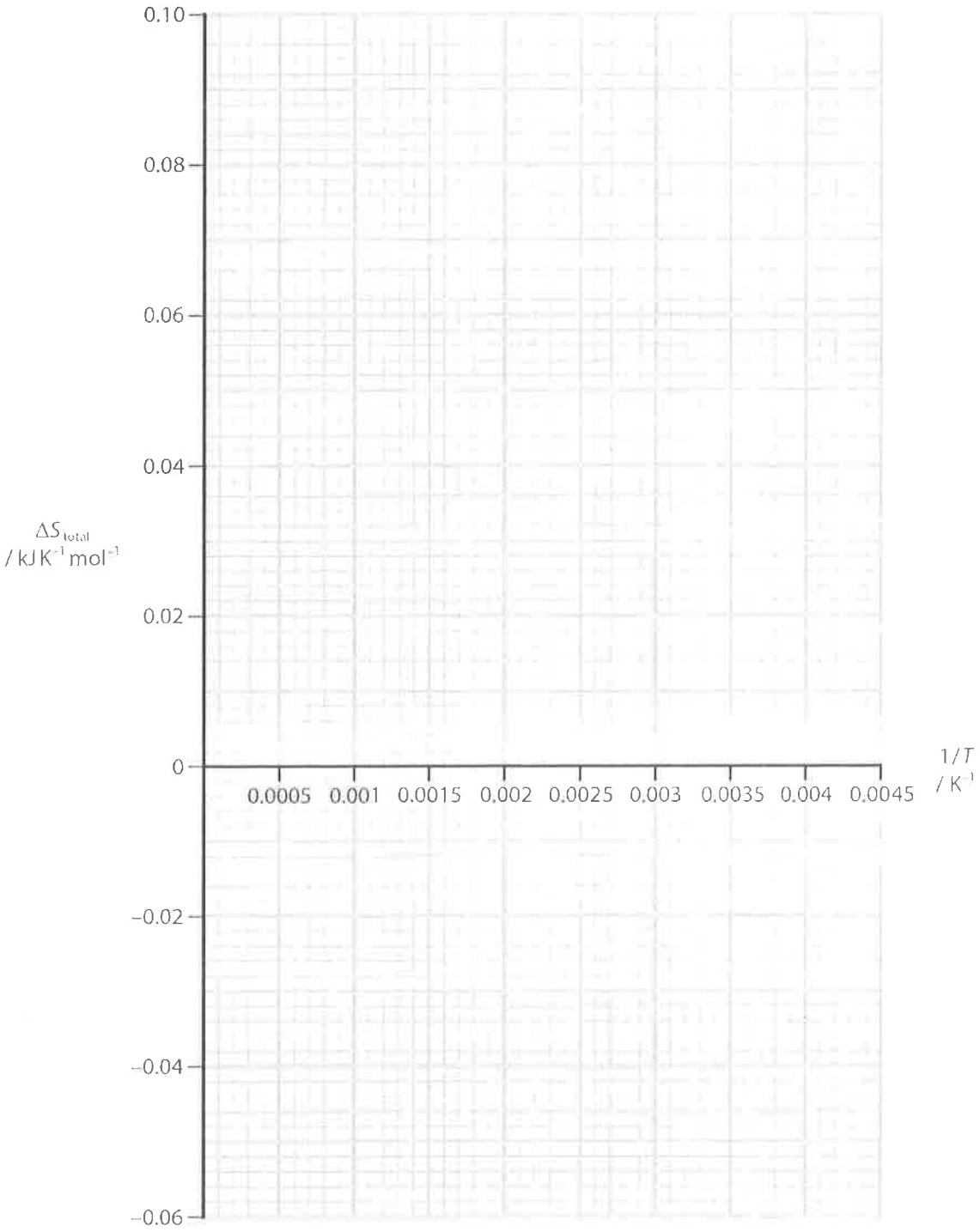
(2)

(b) The value of the total entropy change, ΔS_{total}, varies with temperature.
Data for the value of ΔS_{total} at different temperatures but at standard pressure of 100 kPa are given for this reaction.

Temperature / K	$1/T$ / K^{-1}	ΔS_{total} / $kJ\,K^{-1}mol^{-1}$
250	4.00×10^{-3}	8.27×10^{-2}
375	2.67×10^{-3}	2.25×10^{-2}
500	2.00×10^{-3}	-0.764×10^{-2}
625	1.60×10^{-3}	-2.57×10^{-2}
750	1.33×10^{-3}	-3.77×10^{-2}

Plot a graph of ΔS_{total} against $1/T$ on the grid.
Include a line of best fit.

(3)


0.10
0.08
0.06
0.04
0.02
0
−0.02
−0.04
−0.06
ΔS_{total} / kJ K^{-1} mol^{-1}
0.0005
0.001
0.0015
0.002
0.0025
0.003
0.0035
0.004
0.0045
1/T / K^{-1}

(c) The relationship between ΔS_{total} and 1/T can be found by combining the two equations:

$$\Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system}$$

and $\Delta S_{surroundings} = -\Delta H/T$

to give $$\Delta S_{total} = -\Delta H \times \frac{1}{T} + \Delta S_{system}$$

(i) Determine the gradient of the line plotted in (b), including units in your answer.

(2)

(ii) Identify the thermodynamic quantity that can be obtained from this gradient.

(1)

.....

(iii) Determine the temperature at which the reaction ceases to be thermodynamically feasible at a pressure of 100 kPa.

(1)

.....

(d) The industrial synthesis of ammonia

$$\tfrac{1}{2}N_2(g) + 1\tfrac{1}{2}H_2(g) \rightleftharpoons NH_3(g)$$

is carried out at pressures of about 20000 kPa and temperatures between 700 K and 750 K. These temperatures are higher than the answer to (c)(iii).

(i) State the relationship between the total entropy, ΔS_{total}, and the equilibrium constant, K.

(1)

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(ii) Calculate the value of the equilibrium constant K at 750 K.
Given: ΔS_{total} at 750 K = $-37.7\ J\ K^{-1}\ mol^{-1}$

(2)

(iii) Explain why ΔS_{total} decreases with an increase in temperature.

(3)

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(e) Ammonia from the Haber Process reacts with acids.
With phosphoric acid, H_3PO_4, a number of products are formed in solution. One of these is the fertiliser diammonium hydrogenphosphate.
Write an equation for the production of this fertiliser. State symbols are not required.

(2)

(Total for Question 21 = 17 marks)
TOTAL FOR SECTION C = 17 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8) (18)
							1.0 H hydrogen 1										4.0 He helium 2
(1)	(2)		Key									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4		relative atomic mass atomic symbol name atomic (proton) number									10.8 B boron 5	12.0 C carbon 6	14.0 N nitrogen 7	16.0 O oxygen 8	19.0 F fluorine 9	20.2 Ne neon 10
23.0 Na sodium 11	24.3 Mg magnesium 12	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	27.0 Al aluminium 13	28.1 Si silicon 14	31.0 P phosphorus 15	32.1 S sulfur 16	35.5 Cl chlorine 17	39.9 Ar argon 18
39.1 K potassium 19	40.1 Ca calcium 20	45.0 Sc scandium 21	47.9 Ti titanium 22	50.9 V vanadium 23	52.0 Cr chromium 24	54.9 Mn manganese 25	55.8 Fe iron 26	58.9 Co cobalt 27	58.7 Ni nickel 28	63.5 Cu copper 29	65.4 Zn zinc 30	69.7 Ga gallium 31	72.6 Ge germanium 32	74.9 As arsenic 33	79.0 Se selenium 34	79.9 Br bromine 35	83.8 Kr krypton 36
85.5 Rb rubidium 37	87.6 Sr strontium 38	88.9 Y yttrium 39	91.2 Zr zirconium 40	92.9 Nb niobium 41	95.9 Mo molybdenum 42	[98] Tc technetium 43	101.1 Ru ruthenium 44	102.9 Rh rhodium 45	106.4 Pd palladium 46	107.9 Ag silver 47	112.4 Cd cadmium 48	114.8 In indium 49	118.7 Sn tin 50	121.8 Sb antimony 51	127.6 Te tellurium 52	126.9 I iodine 53	131.3 Xe xenon 54
132.9 Cs caesium 55	137.3 Ba barium 56	138.9 La* lanthanum 57	178.5 Hf hafnium 72	180.9 Ta tantalum 73	183.8 W tungsten 74	186.2 Re rhenium 75	190.2 Os osmium 76	192.2 Ir iridium 77	195.1 Pt platinum 78	197.0 Au gold 79	200.6 Hg mercury 80	204.4 Tl thallium 81	207.2 Pb lead 82	209.0 Bi bismuth 83	[209] Po polonium 84	[210] At astatine 85	[222] Rn radon 86
[223] Fr francium 87	[226] Ra radium 88	[227] Ac* actinium 89	[261] Rf rutherfordium 104	[262] Db dubnium 105	[266] Sg seaborgium 106	[264] Bh bohrium 107	[277] Hs hassium 108	[268] Mt meitnerium 109	[271] Ds darmstadtium 110	[272] Rg roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 Ce cerium 58	141 Pr praseodymium 59	144 Nd neodymium 60	[147] Pm promethium 61	150 Sm samarium 62	152 Eu europium 63	157 Gd gadolinium 64	159 Tb terbium 65	163 Dy dysprosium 66	165 Ho holmium 67	167 Er erbium 68	169 Tm thulium 69	173 Yb ytterbium 70	175 Lu lutetium 71
* Actinide series	232 Th thorium 90	[231] Pa protactinium 91	238 U uranium 92	[237] Np neptunium 93	[242] Pu plutonium 94	[243] Am americium 95	[247] Cm curium 96	[245] Bk berkelium 97	[251] Cf californium 98	[254] Es einsteinium 99	[253] Fm fermium 100	[256] Md mendelevium 101	[254] No nobelium 102	[257] Lr lawrencium 103

SECTION A

Answer ALL the questions in this section.
You should aim to spend no more than 20 minutes on this section.
For each question, select one answer from A to D and put a cross in the box.
If you change your mind, put a line through ☒ the box and then mark your new answer with a cross. ☒

1. Ammonium nitrate is very soluble in water.

$$NH_4NO_3(s) + aq \rightarrow NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H = +25.8\,kJ\,mol^{-1}$$

What is the best explanation for this?

☐ **A** all ammonium salts are soluble in water
☐ **B** the activation energy of the reaction is very low
☐ **C** the enthalpies of hydration of the ions are very exothermic
☒ **D** the entropy change of the system, ΔS_{system} , is positive

(1) ✓

(Total for Question 1 = 1 mark)

2. The standard molar entropy, S, of a substance

☐ **A** is not affected by changes of state or changes in temperature
☐ **B** only changes when the temperature changes
☐ **C** only changes when the substance changes state
☒ **D** changes when the temperature changes and when the substance changes state

(1) ✓

(Total for Question 2 = 1 mark)

3. At 25 °C, the pH of pure water is 7.00 and at 100 °C, the pH of pure water is 6.14.
What can be deduced from this information?

		Enthalpy change of dissociation of water	Concentration of hydrogen ions
☒	A	endothermic	higher at 100 °C than at 25 °C
☐	B	endothermic	lower at 100 °C than at 25 °C
☐	C	exothermic	higher at 100 °C than at 25 °C
☐	D	exothermic	lower at 100 °C than at 25 °C

(1) ✓

(Total for Question 3 = 1 mark)

4. The equation for the precipitation of lead(II) chloride is shown.

$$Pb^{2+}(aq) + 2Cl^{-}(aq) \rightleftharpoons PbCl_2(s)$$

What are the units of the equilibrium constant, Kc?

- ☒ **A** $dm^{9}.mol^{-3}$
- ☐ **B** $dm^{6}.mol^{-2}$
- ☐ **C** $mol^{2}.dm^{-6}$
- ☐ **D** $mol^{3}.dm^{-9}$

(Total for Question 4 = 1 mark)

5. The reaction shown is at equilibrium. The forward reaction is endothermic.

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

(a) Which will **increase** when the temperature is lowered?

(1)

- ☒ **A** the mole fraction of carbon dioxide
- ☐ **B** the partial pressure of carbon monoxide
- ☐ **C** the rate of the backward reaction
- ☐ **D** the value of Kp for the forward reaction

(b) At 680 °C and 1 atm, 52.6 % of the molecules in the gas mixture are carbon monoxide. What is the partial pressure of carbon dioxide, in atmospheres?

(1)

- ☐ **A** 0.237
- ☐ **B** 0.263
- ☒ **C** 0.474
- ☐ **D** 0.526

(Total for Question 5 = 2 marks)

6. Experimental lattice energy values determined using the Born-Haber cycle often differ from calculated theoretical values. The ionic radii and charges of some ions are shown.
P, Q, R and S are **not** the chemical symbols of the elements.

Ion	Ionic radius / nm
P^+	0.076
Q^+	0.167
R^-	0.133
S^-	0.220

Which of these compounds would be expected to show the largest percentage difference between the experimental and theoretical lattice energies?

- ☐ A **PR**
- ☒ B **PS**
- ☐ C **QR**
- ☐ D **QS**

(Total for Question 6 = 1 mark)

7. A series of experiments was carried out to determine the rate constant, k, of the reaction between bromate(V) ions and bromide ions at different temperatures, T.
A graph of $\ln k$ was plotted against $1/T$. The gradient of the line was −4670 K.
The Arrhenius equation may be written as

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + constant \qquad R = 8.31\, J\, mol^{-1} K^{-1}$$

What is the activation energy of this reaction?

- ☒ A $+38.8\, kJmol^{-1}$
- ☐ B $+38.8\, J\, mol^{-1} K^{-1}$
- ☐ C $+562\, Jmol^{-1}$
- ☐ D $+562\, Jmol^{-1} K^{-1}$

(Total for Question 7 = 1 mark)

8. Solid vanadium(V) oxide catalyses the equilibrium shown.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196\,kJ\,mol^{-1}$$

Which statement is correct?

- ☐ **A** vanadium(V) oxide is a homogeneous catalyst
- ☐ **B** decreasing the pressure would increase the equilibrium yield of sulfur trioxide
- ☐ **C** increasing the surface area of the catalyst would increase the equilibrium yield of sulfur trioxide
- ☒ **D** decreasing the temperature would increase the equilibrium yield of sulfur trioxide

(Total for Question 8 = 1 mark)

9. What is the pH of a $0.27\,mol\,dm^{-3}$ aqueous solution of sodium hydroxide?
[$K_w = 1.0 \times 10^{-14}\,mol^2\,dm^{-6}$ at 298 K]

- ☐ **A** 0.57
- ☒ **B** 13.43
- ☐ **C** 13.73
- ☐ **D** 14.57

(Total for Question 9 = 1 mark)

10. Propanone reacts with iodine in the presence of a sulfuric acid catalyst.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

The rate equation for this reaction is:

$$\text{rate} = k[H^+][CH_3COCH_3]$$

Two experiments were carried out. In both experiments the concentration of propanone and iodine remained the same but the concentration of the sulfuric acid was changed.
The initial rate in the first experiment was three times faster than the initial rate in the second experiment.
In the first experiment the initial pH was 1.50
What is the initial pH in the second experiment?

- ☐ **A** 1.02
- ☒ **B** 1.98
- ☐ **C** 2.28
- ☐ **D** 4.50

(Total for Question 10 = 1 mark)

11. The water gas reaction is used in the manufacture of hydrogen.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad \Delta H = +131.2 kJ\,mol^{-1}$$

(a) What is the equilibrium constant, K_c, for this reaction?

(1)

☒ A $K_c = [CO][H_2]$

☐ B $K_c = \dfrac{[CO][H_2]}{[C]}$

(1) ✓ ☒ C $K_c = \dfrac{[CO][H_2]}{[H_2O]}$

☐ D $K_c = \dfrac{[CO][H_2]}{[H_2O][C]}$

(b) What happens to the equilibrium constants of the forward and reverse reactions when the temperature is **increased**?

(1)

		K_c of forward reaction	K_c of reverse reaction
☐	A	increases	increases
(1) ✓ ☒	B	increases	decreases
☐	C	decreases	increases
☐	D	decreases	decreases

(Total for Question 11 = 2 marks)

12. The total entropy change, ΔS_{total}, of a reaction at 298 K is $-85.0\,J\,K^{-1}mol^{-1}$.

What is the value of the equilibrium constant for this reaction at 298 K?

[$R = 8.31\,J\,mol^{-1}K^{-1}$]

(1) ✓ ☒ A 3.61×10^{-5}

☐ B 9.07×10^{-1}

☐ C 9.66×10^{-1}

☐ D 2.77×10^{4}

(Total for Question 12 = 1 mark)

13. When ethanoic acid and chloroethanoic acid are mixed, an equilibrium is set up.

$$CH_3COOH + CH_2ClCOOH \rightleftharpoons CH_3COOH_2^+ + CH_2ClCOO^-$$

The Brønsted-Lowry acids in this equilibrium are

- ☐ **A** CH_3COOH and $CH_2ClCOOH$
- ☐ **B** CH_3COOH and $CH_3COOH_2^+$
- ☒ **C** $CH_2ClCOOH$ and $CH_3COOH_2^+$
- ☐ **D** $CH_3COOH_2^+$ and CH_2ClCOO^-

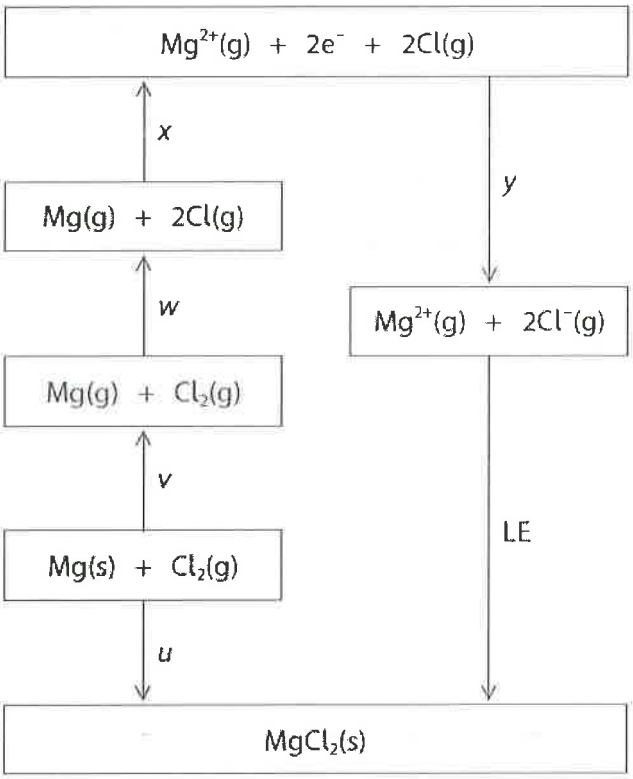
(Total for Question 13 = 1 mark)

14. An ionic solid dissolves in water.
Which of the following statements about the signs of these standard enthalpy changes is possible?

	$\Delta H^{\ominus}_{solution}$	$\Delta H^{\ominus}_{hydration}$	Lattice energy
☐ **A**	negative	negative	positive
☒ **B**	positive	negative	negative
☐ **C**	negative	positive	negative
☐ **D**	positive	positive	positive

(Total for Question 14 = 1 mark)

15. The diagram shows the Born-Haber cycle for magnesium chloride.



(a) Which of these is the electron affinity of chlorine?

(1)

- ☐ **A** y
- ☒ **B** y/2
- ☐ **C** (w + y)
- ☐ **D** (w + y)/2

(b) Which expression gives the lattice energy (LE) for magnesium chloride?

(1)

- ☒ **A** LE = $u - (v + w + x + y)$
- ☐ **B** LE = $v + w + x + y - u$
- ☐ **C** LE = $y - u - (v + w + x)$
- ☐ **D** LE = $v + w + x - y + u$

(c) Which energy change in the cycle does *x* represent?

(1)

☐ **A** the first ionisation energy of magnesium
☐ **B** the second ionisation energy of magnesium
(1) ✓ ☒ **C** the sum of the first and second ionisation energies of magnesium
☐ **D** the sum of the enthalpy change of atomisation and the first and second ionisation energies of magnesium

(Total for Question 15 = 3 marks)

16. The decomposition of hydrogen iodide at 500 K is an equilibrium reaction.
The equilibrium can be written as two different equations.

Equation 1 $HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$ $\Delta H_1 = +5\,kJ\,mol^{-1}$ $K_{c_1} = 6 \times 10^{-3}$

Equation 2 $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ ΔH_2 $Equilibrium\,constant = K_{c_2}$

Which combination of expressions is correct?

☐ **A** $\Delta H_1 = \Delta H_2$ and $K_{c_1} = K_{c_2}$
☐ **B** $\Delta H_1 = \frac{1}{2}\Delta H_2$ and $K_{c_1} = \frac{1}{2} K_{c_2}$
☐ **C** $\Delta H_1 = \sqrt{\Delta H_2}$ and $K_{c_1} = \sqrt{K_{c_2}}$
(1) ✓ ☒ **D** $\Delta H_1 = \frac{1}{2}\Delta H_2$ and $K_{c_1} = \sqrt{K_{c_2}}$

(Total for Question 16 = 1 mark)

17. Which reaction has an enthalpy change equal to the enthalpy change of solution of potassium chloride?

☐ **A** 1 mol KCl(s) + 2 mol of $H_2O(l)$ → $K^+(aq)$ + $Cl^-(aq)$
(1) ✓ ☒ **B** 1 mol KCl(s) + excess $H_2O(l)$ → $K^+(aq)$ + $Cl^-(aq)$
☐ **C** 1 mol KCl(g) + 2 mol of $H_2O(l)$ → $K^+(aq)$ + $Cl^-(aq)$
☐ **D** 1 mol KCl(g) + excess $H_2O(l)$ → $K^+(aq)$ + $Cl^-(aq)$

(Total for Question 17 = 1 mark)

TOTAL FOR SECTION A = 21 MARKS

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

18. The kinetics of the reaction between hydrogen peroxide and iodide ions in the presence of sulfuric acid is investigated.

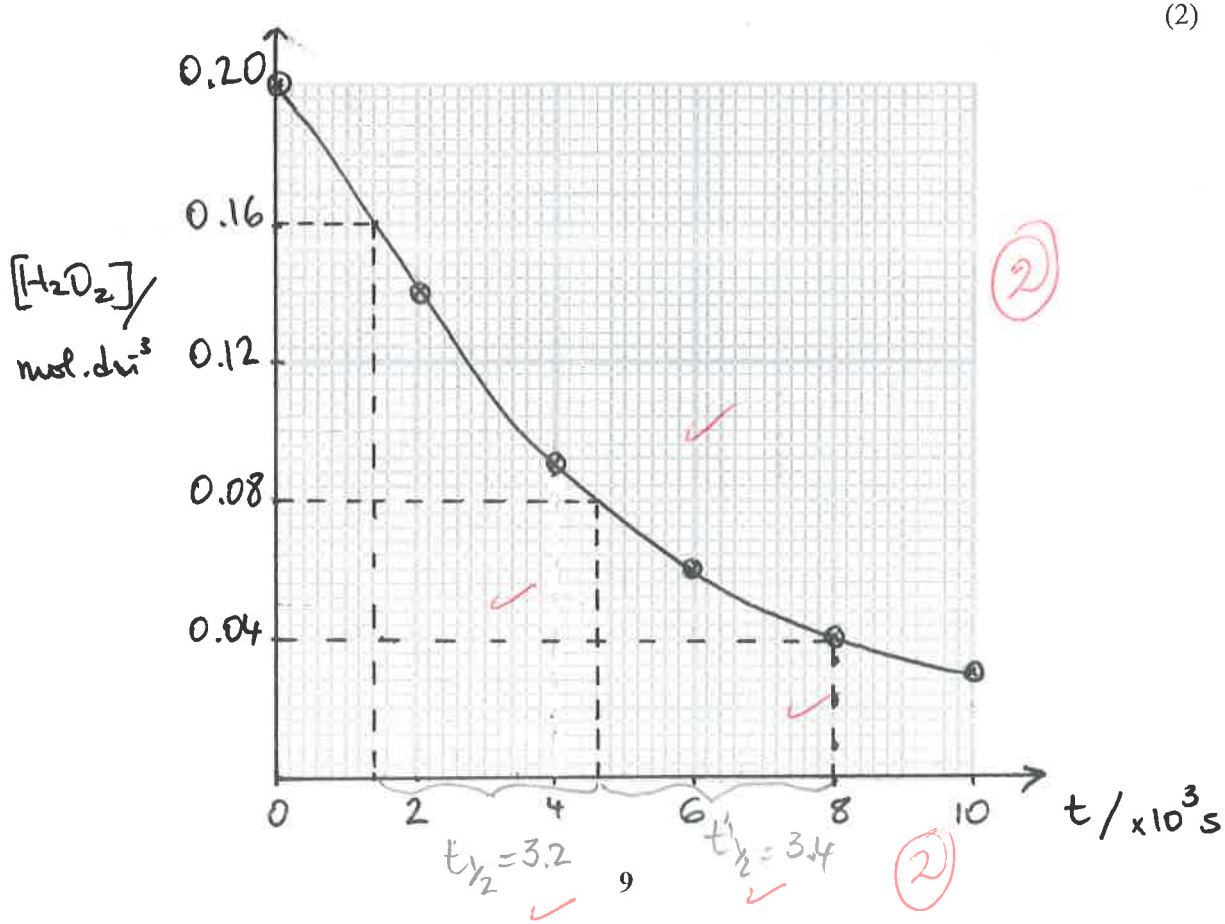
$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

(a) First, the concentration of hydrogen peroxide is measured at different times, while keeping the concentrations of iodide and hydrogen ions constant. The following results are obtained.

$t / 10^3 s$	$[H_2O_2]$ / mol dm^{-3}
0	0.20
2	0.14
4	0.09
6	0.06
8	0.04
10	0.03

(i) Plot a graph of $[H_2O_2]$ / mol dm^{-3} against t / 10^3s.

(2)



(ii) Find **two** successive half-lives from your graph.
Show your working on your graph, together with their values.

$t_{1/2} = 3.2 \times 10^3 s$ $t'_{1/2} = 3.4 \times 10^3 s$. (2)

(iii) Deduce the order of the reaction with respect to hydrogen peroxide. Justify your answer.

(2)

The two half-lives values are concordant ✓1 hence it's a first order reaction with respect to H_2O_2 ✓1

(b) The experiment is repeated using an initial rate method.
Mixtures are prepared using $0.10 mol\ dm^{-3}$ solutions of each reactant, $2 cm^3$ of sodium thiosulfate solution mixed with starch and varying amounts of water so that the total volume is always $12 cm^3$.
The time for the mixtures to change colour is recorded and the initial rate calculated.

Run	Volume KI /cm^3	Volume H_2O_2 /cm^3	Volume H_2SO_4 /cm^3	Volume of water /cm^3	Initial rate /mol dm^{-3} s^{-1}
1	3.0	3.0	3.0	1.0	1.06×10^{-4}
2	2.0	3.0	3.0	2.0	7.00×10^{-5}
3	1.0	3.0	3.0	3.0	3.50×10^{-5}
4	3.0	3.0	2.0	2.0	1.08×10^{-4}
5	3.0	3.0	1.0	3.0	1.05×10^{-4}

(i) The reciprocal of time can be used as an approximate measure of rate.
What assumption does this approximation depend on?

(1)

The reaction is considered to have a rate that does not change significantly ✓1 over the time of its measurement. ✓

(ii) Use the results in the table to deduce the order of reaction with respect to iodide ions and hydrogen ions.
Justify each answer by referring to relevant data from the table.

(3)

Iodide ions ... using experiments 1 & 3, as $[I^-]$ dropped by a third, so did the initial rate while the other reagents' concentrations remained constant. (2)
=> it's a first order with respect to I^-. ✓

Hydrogen ions ... using experiments 4 & 5, as $[H^+]$ halved the initial remained constant, (1)
so was the concentration of the other species
=> it's a zero order with respect to H^+. ✓

(iii) Write the overall rate equation for this reaction using your answers to (a)(iii) and (b)(ii).

(1)

$r = k[I^-][H_2O_2]$ ✓ (1)

(iv) Calculate the actual concentrations of hydrogen peroxide and iodide ions in the **mixture** used in Run 1 from the table in (b).

(1)

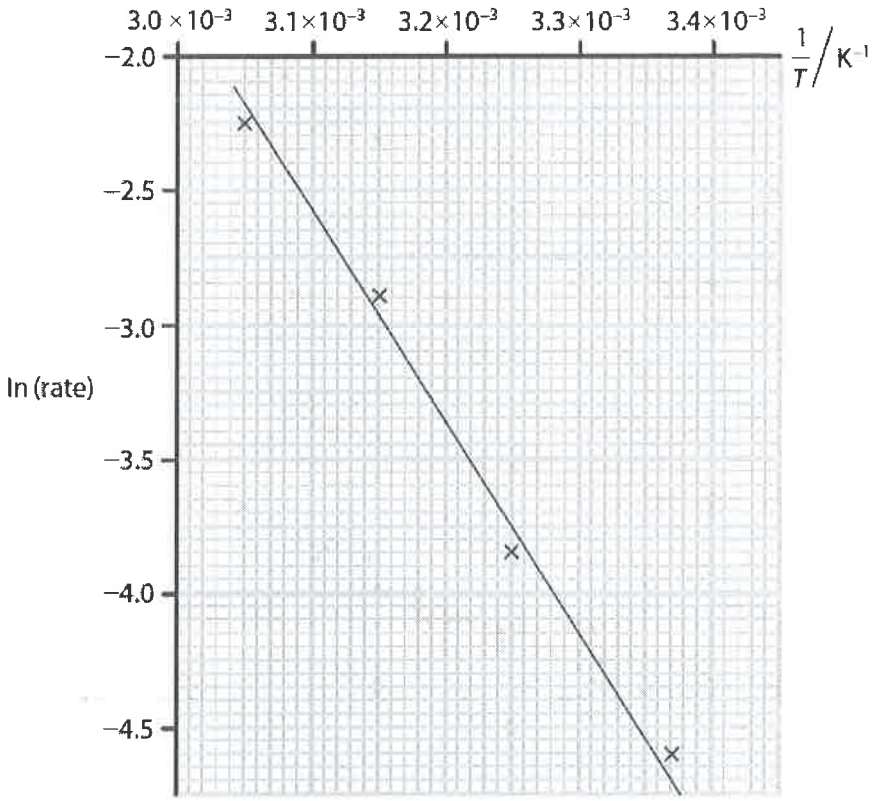
$$[H_2O_2] = [I^-] = \frac{3 \times 10^{-3} \times 0.1}{12 \times 10^{-3}} = 2.5 \times 10^{-2} \text{ mol.dm}^{-3}$$ ✓ (1)

(v) Calculate a value for the rate constant using Run 1 from the table in (b) and your answers to parts (b)(iii) and (b)(iv). Include units for the rate constant.

(2)

$$k = \frac{1.06 \times 10^{-4}}{(2.5 \times 10^{-2})^2} = 0.170 \text{ mol}^{-1}.\text{dm}^3.\text{s}^{-1}$$ ✓ (1) ✓ (1)

(c) (i) The activation energy for this reaction is found by keeping the concentrations of reactants constant and repeating the reaction at different temperatures.
A graph of $\ln(rate)$ of the reaction against reciprocal of temperature is given below.



Calculate the gradient of the graph.
Use your value of the gradient and the equation below to calculate the activation energy of the reaction.

$$\ln(rate) = -\frac{E_a}{R} \times \frac{1}{T} + constant \qquad [\ R = 8.31\ J\,K^{-1}\,mol^{-1}\ ]$$

Include a sign and units with your answer.

(3)

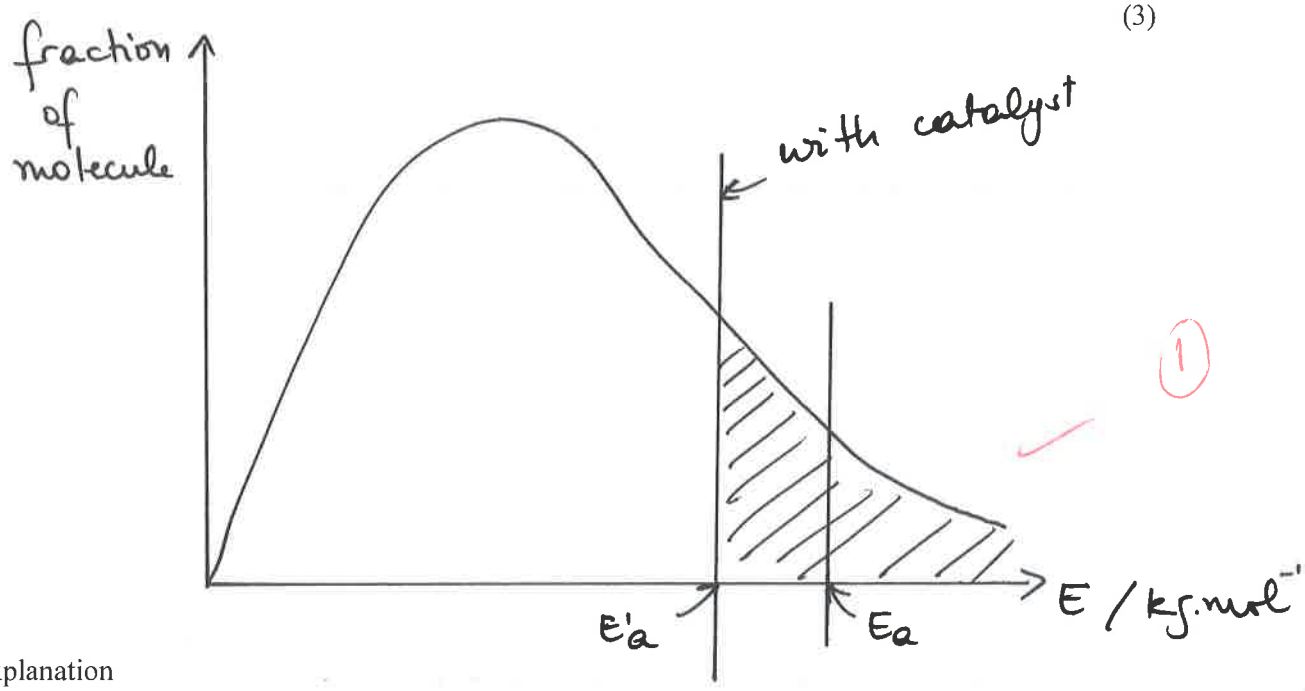
$$-\frac{Ea}{R} = \frac{-2.2 + 4.55}{3.05 \times 10^{-3} - 3.35 \times 10^{-3}} = \frac{2.35 \times 10^{3}}{-0.3}$$ ✓(1) ✓(1)

$$\Rightarrow Ea = \frac{8.31 \times 2.35 \times 10^{3}}{0.3} = +\ 65095\ J.mol^{-1}$$

$$\Rightarrow Ea = +\ 65\ kJ.mol^{-1}$$ ✓(1)

*(ii) If the same reaction is carried out in the presence of a catalyst of ammonium molybdate, the activation energy is found to be much lower.
Sketch a Maxwell-Boltzmann distribution of molecular energies.
Use your sketch to explain why this reduction in activation energy increases the rate of the reaction.

(3)



Explanation

The area past the value of E'a, under the curve increases in the presence of catalyst => more successful collisions => faster rate

(Total for Question 18 = 20 marks)

19. This question is about ammonia and ammonium chloride.

(a) Ammonia is produced by reacting nitrogen and hydrogen as shown.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) Write the expression for the equilibrium constant, K_p.

(1)

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3} \quad @ \text{ eqm.}$$ ✓(1)

(ii) An equilibrium was established by mixing nitrogen and hydrogen in a 1:3 ratio by volume, at a temperature of $450\,°C$ and pressure of $200\,atm$.
The equilibrium mixture contained 28% of ammonia and 18% nitrogen by volume.
Complete the table.

(2)

Substance	Mole fraction	Partial pressure / atm
N_2	0.18	36 ✓
H_2	0.54 ✓	108 ✓
NH_3	0.28	56

(2)

(iii) Calculate the equilibrium constant.
Give your answer to an appropriate number of significant figures and include units, if required.

(2)

$$K_p = \frac{56^2}{36 \times 108^3} = 6.9 \times 10^{-5} \text{ atm}^{-2}$$ ✓(1) ✓(1)

(iv) When the temperature was reduced to 400°C at the same pressure, the equilibrium mixture contained 36% of ammonia.
Explain what can be deduced about this reaction from this information.

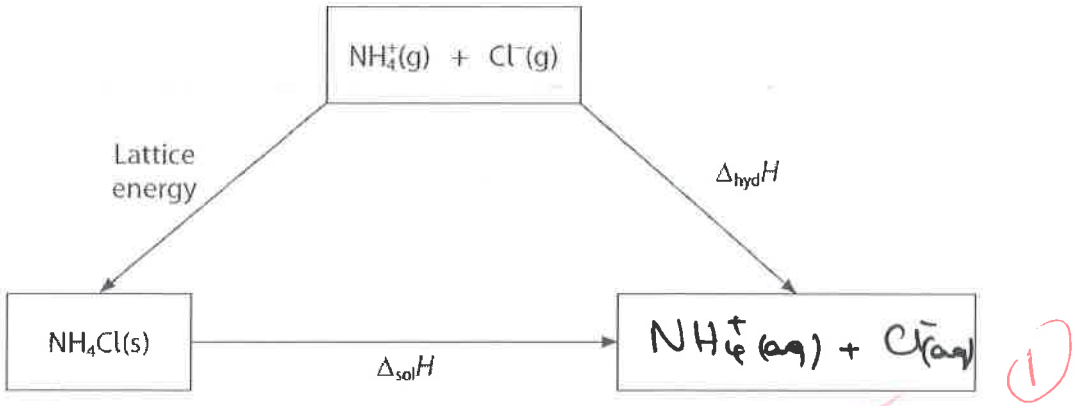
(2)

The decrease of temperature favours the exothermic rxn. ✓(1)
In this case, decreasing temperature increased the mole fraction of NH_3, hence the forward reaction is exothermic. ✓(1)

(b) Ammonium chloride can be produced by reacting ammonia with hydrogen chloride.
Ammonium chloride is a white solid that is very soluble in water.
Hess's Law can be used to calculate the enthalpy of solution of ammonium chloride, using hydration enthalpies and lattice energy.

(i) Complete the Hess cycle by filling in the empty box.

(1)



(1)

(ii) Complete the expression for the enthalpy change of solution using the hydration enthalpies and lattice energy.

(1)

$\Delta_{sol}H =$ - L.E + $\Sigma \Delta_{hyd}H$ [ions] (1)

(iii) Calculate the enthalpy change of solution, using your expression in (b)(ii) and these data.

Enthalpy change of hydration of $NH_4^+ = -307\,kJ\,mol^{-1}$
Enthalpy change of hydration of $Cl^- = -378\,kJ\,mol^{-1}$
Lattice energy of $NH_4Cl = -705\,kJ\,mol^{-1}$

(2)

$\Delta_{sol}H = +705 - 307 - 378$

$= +20\ kJ.mol^{-1}$ (2)

(iv) A student suggested that the enthalpy change of solution of ammonium bromide would be of a similar magnitude to the enthalpy change of solution of ammonium chloride. Comment on this suggestion in terms of the hydration enthalpies and lattice energies of these two compounds.

(3)

* The L.E$_{(NH_4Br)}$ is less exothermic than the L.E$_{(NH_4Cl)}$ as I.R$_{(Br^-)}$ > I.R$_{(Cl^-)}$ ✓ (1)
* As a result to the difference in I.R between Br^- & Cl^-, the $\Delta_{hyd}H_{(Br^-)}$ is less exothermic than $\Delta_{hyd}H_{(Cl^-)}$ which will compensate for the decrease in magnitude of the L.E (1)
* $\Delta_{sol}H = -L.E + \Sigma\Delta_{hyd}H_{[ions]}$ ✓ (1)

=> $\Delta_{sol}H_{[NH_4Br]}$ would be similar to $\Delta_{sol}H_{[NH_4Cl]}$ ✓

(c) Write an **ionic** equation to show why aqueous solutions of ammonium ions are acidic. State symbols are not required.

(1)

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$$ ✓ (1)

(Total for Question 19 = 15 marks)

20. This question is about acids and bases.

(a) State what is meant by a Brønsted-Lowry base.

(1)

A specie accepting a proton (1)

(b) Calculate the concentration of hydrogen ions, in $mol\,dm^{-3}$, in a solution with a pH of 9.43

(1)

$[H^+] = 10^{-pH} = 10^{-9.43} = 3.72 \times 10^{-10}$ mol.dm^{-3} (1)

(c) Write the equation for the dissociation of water.

(1)

$2H_2O \rightleftharpoons H_3O^+ + OH^-$ (1)

(d) Write the expression of K_w.

(1)

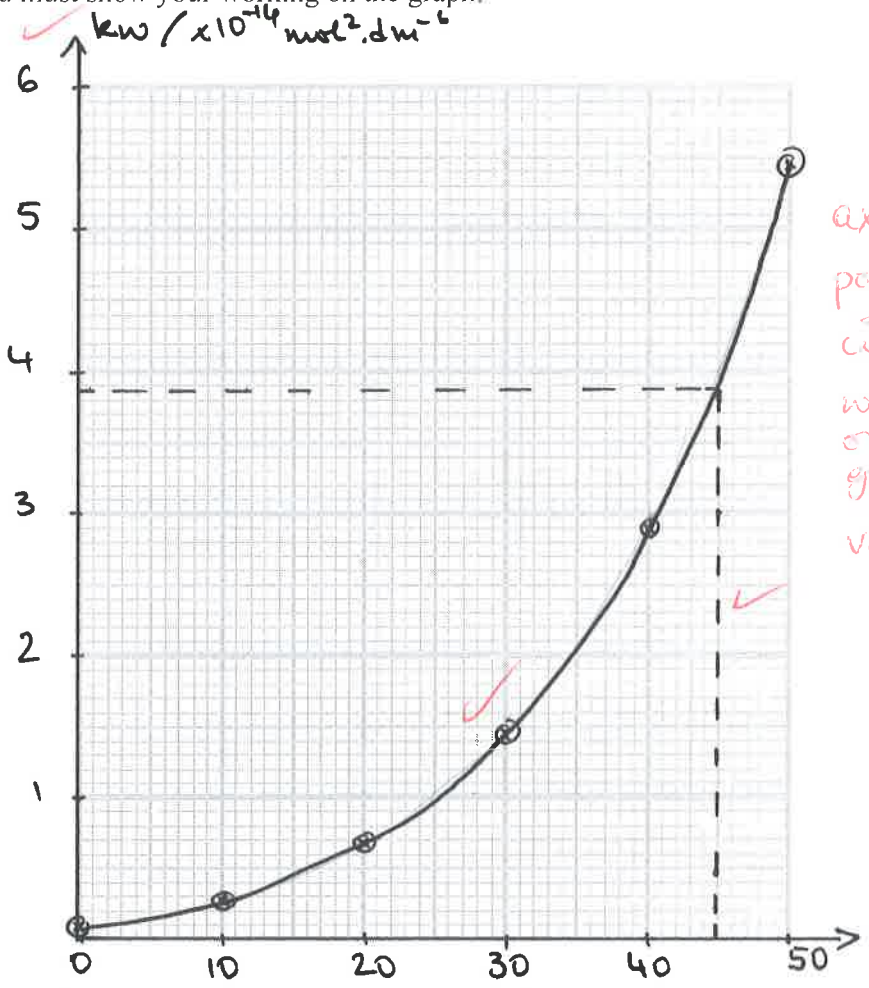
$K_w = [H_3O^+][OH^-]$ (1)

(e) The ionic product of water, K_w, varies with temperature as shown.

Temperature / °C	K_w / mol^2 dm^{-6}
0	0.11×10^{-14}
10	0.29×10^{-14}
20	0.68×10^{-14}
30	1.47×10^{-14}
40	2.92×10^{-14}
50	5.48×10^{-14}

(i) Determine the value of K_w at 45°C by plotting a suitable graph.
You must show your working on the graph.

(4)



axis : (1)
points of curve : (1)
working on graph : (1)
value of kw : (1)

K_w at 45°C = ...3.85.x10^{-14}

(ii) The ionic product of water at 30°C is $1.47 \times 10^{-14}\ mol^2\ dm^{-6}$.
Calculate the pH of water at this temperature.

(3)

$[H^+] = [OH^-]$ in water (1)

$\Rightarrow [H^+]^2 = 1.47 \times 10^{-14}$

$\Rightarrow [H^+] = \sqrt{1.47 \times 10^{-14}}$ (1)

$\Rightarrow [H^+] = 1.21 \times 10^{-7}$

$\Rightarrow pH = 6.92$ (1)

(f) Calculate the pH of the solution formed when $51.2\,cm^3$ of $0.927\,mol\,dm^{-3}$ NaOH(aq) is mixed with $40.4\,cm^3$ of $0.370\,mol\,dm^{-3}$ H_2SO_4(aq).
[Ionic product of water $K_w = 1.00 \times 10^{-14}\,mol^2\,dm^{-6}$]

(6)

$2\,NaOH + H_2SO_4 \longrightarrow 2H_2O + Na_2SO_4$

$n_{NaOH} = 47.46 \times 10^{-3}$ mol (1)

$n_{H_2SO_4} = 40.4 \times 10^{-3} \times 0.370 = 14.95 \times 10^{-3}$ mol (1)

but NaOH : H_2SO_4

is 2 : 1 $\Rightarrow n_{NaOH}$ (needed) $= 2 \times 14.95 \times 10^{-3}$ (1)

$= 29.9 \times 10^{-3}$ mol

$\Rightarrow n_{NaOH}$ (remaining) $= 47.46 \times 10^{-3} - 29.9 \times 10^{-3}$

$= 17.56 \times 10^{-3}$ mol (1)

$\Rightarrow [OH^-] = \dfrac{17.56 \times 10^{-3}}{(51.2 + 40.4) \times 10^{-3}} = 0.192\ mol.dm^{-3}$ (1)

$\Rightarrow [H^+] = \dfrac{10^{-14}}{0.192} = 5.21 \times 10^{-14}\ mol.dm^{-3}$

$\Rightarrow pH = 13.28$ (1)

(Total for Question 20 = 17 marks)
TOTAL FOR SECTION B = 52 MARKS

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

21. The equation for the formation of ammonia in the Haber Process is shown

$$\tfrac{1}{2}N_2(g) + 1\tfrac{1}{2}H_2(g) \rightleftharpoons NH_3(g)$$

(a) At 298K the standard entropy change of the system, $\Delta S^{\ominus}_{system} = -98\,J\,K^{-1}mol^{-1}$.

Calculate the standard entropy of one mole of ammonia.
Use the value of $\Delta S^{\ominus}_{system}$ and the data in the table.

Substance	Standard molar entropy, $S^{\ominus}$ / $JK^{-1}mol^{-1}$
N_2	192
H_2	131

$$\Delta S_{sys} = S^{\ominus}_{NH_3} - \left[\tfrac{1}{2}S^{\ominus}_{N_2} + \tfrac{3}{2}S^{\ominus}_{H_2}\right] \quad (1)$$ (2)

$$\Rightarrow S^{\ominus}_{NH_3} = \Delta S_{sys} + \tfrac{1}{2}S^{\ominus}_{N_2} + \tfrac{3}{2}S^{\ominus}_{H_2}$$

$$= -98 + \tfrac{1}{2}\times 192 + \tfrac{3}{2}\times 131$$

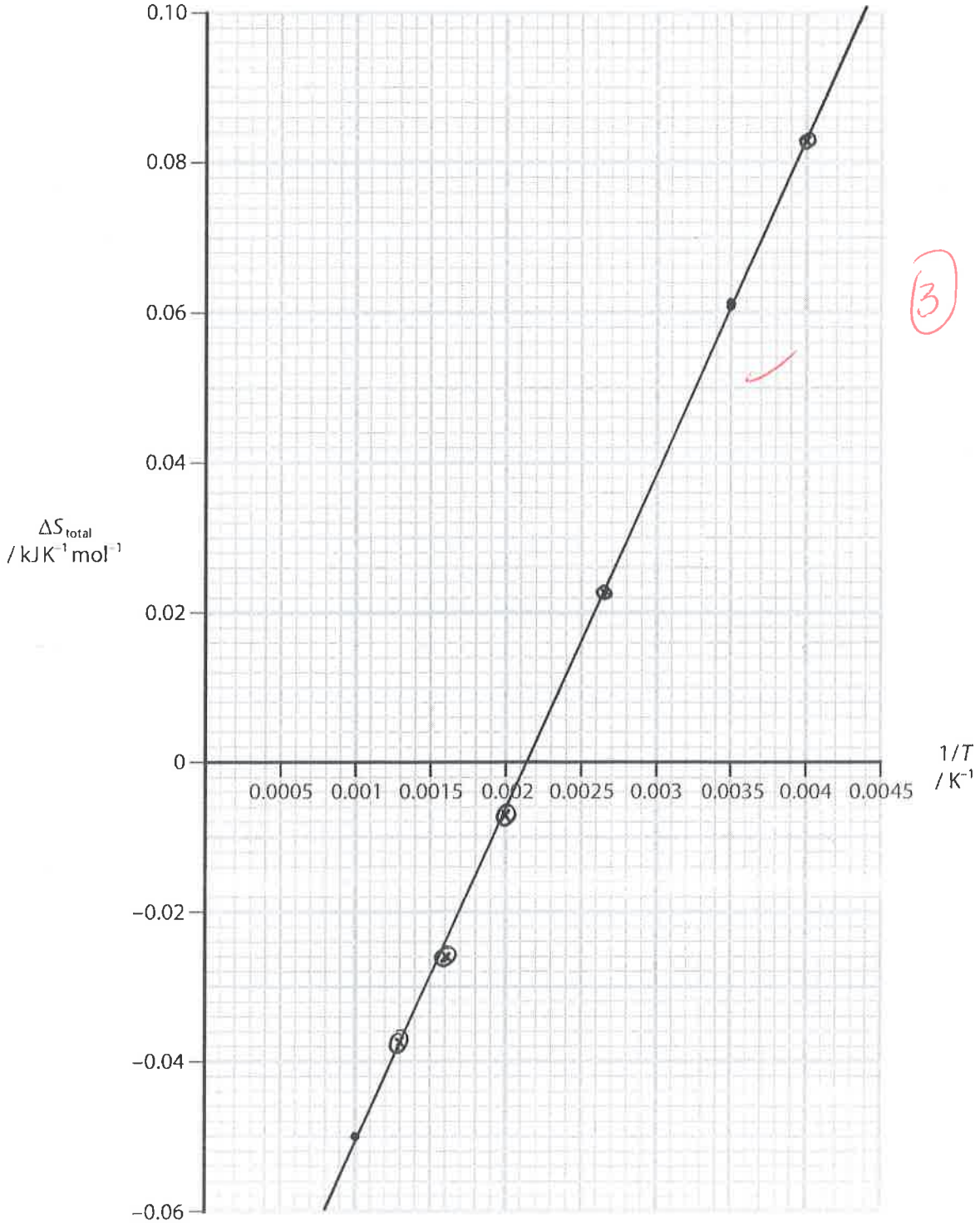
$$\Rightarrow S^{\ominus}_{NH_3} = +194.5\ J.mol^{-1}.K^{-1} \quad (1)$$

(b) The value of the total entropy change, ΔS_{total}, varies with temperature.
Data for the value of ΔS_{total} at different temperatures but at standard pressure of 100 kPa are given for this reaction.

Temperature / K	1/T / K^{-1}	ΔS_{total} / $kJ\,K^{-1}mol^{-1}$
250	4.00×10^{-3}	8.27×10^{-2}
375	2.67×10^{-3}	2.25×10^{-2}
500	2.00×10^{-3}	-0.764×10^{-2}
625	1.60×10^{-3}	-2.57×10^{-2}
750	1.33×10^{-3}	-3.77×10^{-2}

Plot a graph of ΔS_{total} against 1/T on the grid.
Include a line of best fit.

(3)


0.10
0.08
0.06
0.04
0.02
0
−0.02
−0.04
−0.06
ΔS total / kJ K⁻¹ mol⁻¹
0.0005
0.001
0.0015
0.002
0.0025
0.003
0.0035
0.004
0.0045
1/T / K⁻¹

3

(c) The relationship between ΔS_{total} and 1/T can be found by combining the two equations:

$$\Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system}$$

and $\Delta S_{surroundings} = -\Delta H/T$

to give $$\Delta S_{total} = -\Delta H \times \frac{1}{T} + \Delta S_{system}$$

(i) Determine the gradient of the line plotted in (b), including units in your answer. (2)

(0.0035 ; 0.061) (0.001 ; −0.05)

$$m = \frac{0.061 + 0.05}{0.0035 - 0.001} = +44.4 \text{ kJ.mol}^{-1}$$ ✓1 ✓1

units : $\frac{\text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}{\text{K}^{-1}}$

(ii) Identify the thermodynamic quantity that can be obtained from this gradient. (1)

It's ΔH ✓1

(iii) Determine the temperature at which the reaction ceases to be thermodynamically feasible at a pressure of 100 kPa. (1)

$\Delta S_T = 0$ @ $\frac{1}{T} = 0.00215$ ✓ $\Rightarrow T > 465$ K. ✓1

(d) The industrial synthesis of ammonia

$$\tfrac{1}{2}N_2(g) + 1\tfrac{1}{2}H_2(g) \rightleftharpoons NH_3(g)$$

is carried out at pressures of about 20000 kPa and temperatures between 700 K and 750 K. These temperatures are higher than the answer to (c)(iii).

(i) State the relationship between the total entropy, ΔS_{total}, and the equilibrium constant, K. (1)

$\Delta S_T = R \ln K$ ✓ or $K = e^{\frac{\Delta S_T}{R}}$ ✓1

(ii) Calculate the value of the equilibrium constant K at 750 K.
Given: ΔS_{total} at 750 K = $-37.7\ J\ K^{-1} mol^{-1}$

(2)

$K = e^{\frac{-37.7}{8.31}} = 0.011$ ✓ (2)

(iii) Explain why ΔS_{total} decreases with an increase in temperature.

(3)

$\Delta S_T = \Delta S_{sys} - \frac{\Delta H}{T}$

but $\Delta H < 0 \Rightarrow -\frac{\Delta H}{T} > 0$ ✓ (1)

& ΔS_{sys} is constant as $T \uparrow$.

If $T \uparrow \Rightarrow -\frac{\Delta H}{T}$ becomes less positive (1)

hence ΔS_T also decreases ✓ (1)

(e) Ammonia from the Haber Process reacts with acids.
With phosphoric acid, H_3PO_4, a number of products are formed in solution. One of these is the fertiliser diammonium hydrogenphosphate.
Write an equation for the production of this fertiliser. State symbols are not required.

(2)

$2NH_3 + H_3PO_4 \longrightarrow (NH_4)_2HPO_4$ (2)

(Total for Question 21 = 17 marks)
TOTAL FOR SECTION C = 17 MARKS
TOTAL FOR PAPER = 90 MARKS